



tional groups activity coefficient) as presented by Prausnitz et al. [11]. In application of the UNIFAC model, van der Waals surface and volume size parameters as well as interaction parameters between different functional groups are required. As these parameters have not been reported for the functional groups involved in NMP according to Reid et al. [13], the size and energy parameters for this solvent with the other functional groups in the model molecules have been obtained in this work and used in the liquid-liquid equilibrium calculations.

## 2 Experimental

The sample which has been used here for illustration of the above mentioned method is the lube-oil cut SAE 10 (on the scale of the Society of Automotive Engineers) of the Tehran Refinery.

Several experiments at 50 and 42 °C and 1 atm pressure with different ratio of solvent to oil have been carried out in a batch mixer-settler (see Fig. 1) for extracting aromatic components from the lube-oil cut SAE 10 of the Tehran Refinery by the solvent *N*-methylpyrrolidone. Equilibrium composition of the resultant phases, i.e., raffinate and extract have been obtained after evaporating of solvent from the phases in the rotary evaporator system by measurement of the density by a densitometer Model DMA 48 (Austoria made) with the accuracy of +0.000003 g/cm<sup>3</sup>, refractive index by the standard method of ASTM D1218 with the accuracy of +0.00006 and viscosity using the reliable equations of Riazi [15]. Measured values of these parameters for the lube oil cut have been given in Tab. 1. Moreover, true boiling point (TBP) data of the lube oil cut have been obtained using the Simdis GC Chrompac Model 438 by the standard method of ASTM-2887 [1]. The results of measurements are shown in Tab. 2.

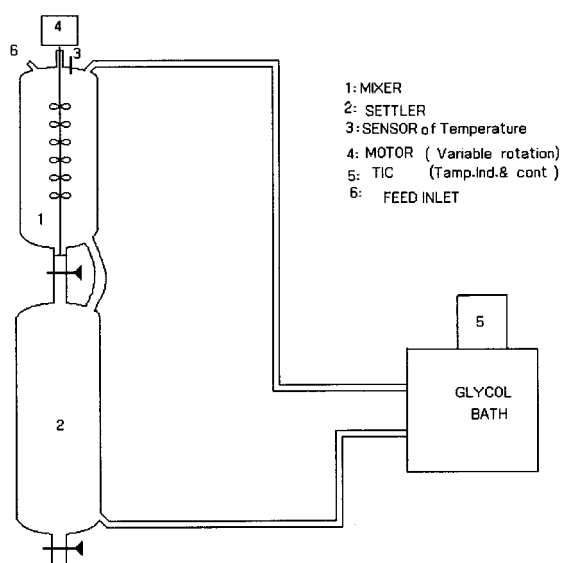


Figure 1. Liquid-Liquid Extractor (Batch Mixer-Settler).

Table 1. Measured properties of the lube-oil cut SAE 10 of Tehran Refinery.

Property	Measured Value
Viscosity ( 40 °C )	32.19 (Centistokes)
Viscosity ( 100 °C )	4.93 (Centistokes)
Specific Gravity ( 60 °F/60 °F )	0.9134
Refractive Index ( 1 atm and 20 °C )	1.5058

Table 2. True Boiling Point (TBP) vs. weight percent of distilled lube-oil cut SAE 10 of Tehran Refinery produced by the Simdis GC Chrompac system Model 438.

Wt%	TBP(°C)	Wt%	TBP(°C)	Wt%	TBP(°C)	Wt%	TBP(°C)
0	281.3	26	377.6	52	399.7	78	418.6
2	308.3	28	379.9	54	401.3	80	420.2
4	324.7	30	381.7	56	402.6	82	421.7
6	335.8	32	383.5	58	404.0	84	423.3
8	344.8	34	385.3	60	405.3	86	425.3
10	350.6	36	387.3	62	406.9	88	427.4
12	356.0	38	389.1	64	408.2	90	429.4
14	359.8	40	390.7	66	409.6	92	431.9
16	363.7	42	392.3	68	411.2	94	435.0
18	367.3	44	393.8	70	412.5	96	438.6
20	370.2	46	395.2	72	413.9	98	444.5
22	372.4	48	396.8	74	415.4	100	464.7
24	375.1	50	398.3	76	416.8		

## 3 Modeling and Calculations

It is evident that a complex mixture such as the lube-oil cut used here can not be directly introduced in the equilibrium calculations, and it must be modeled to several representative molecules. Therefore data of Tab. 2 have been analyzed in order to determine the distribution functions of the lube-oil cut. The experimental methods for determining composition of petroleum fluids are expensive and time consuming and are not proper for engineering applications as it has been pointed out by others [6, 16, 23]. Using the data of Tab. 2 and the general form of a proper distribution function Riazi [14], the molecular weight distribution functions of three main homologue series in the lube-oil cut, i.e., paraffins, naphthenes, and aromatics are presented in the following forms as shown by Vakili-Nezhaad et al. [20]:<sup>1)</sup>

$$W_p(N) = 3.78 \times 10^{-7} (14.0268N - 223.8)^{2.4662} \exp \left[ - \left( \frac{14.0268N - 223.8}{102} \right)^{3.4662} \right] \quad (1)$$

1) List of symbols at the end of the paper.

$$W_n(N) = 5.54 \times 10^{-7} (14.0268N - 209.7)^{2.47} \exp \left[ - \left( \frac{14.0268N - 209.7}{91.43} \right)^{3.47} \right] \quad (2)$$

$$W_a(N) = 7.42 \times 10^{-7} (14.0268N - 201.047)^{2.4575} \exp \left[ - \left( \frac{14.0268N - 201.047}{85} \right)^{3.4575} \right] \quad (3)$$

Therefore the average molecular weights of different homologue series existing in the lube-oil cut are calculated from the Eqs. (1–3). For calculating the average molecular weights of different homologue series, because of the special forms of the above equations, a table of gamma function must be used as shown by Riazi [14]. Using this mathematical table from Spiegel [19], the following values have been obtained by Vakili-Nezhaad et al. [21]:

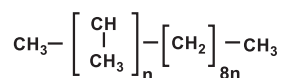
$$MW_p = 328.18 \quad (4)$$

$$MW_n = 291.84 \quad (5)$$

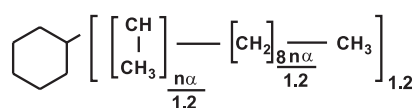
$$MW_a = 271.16 \quad (6)$$

Here we use the method of Ruzicka [17] for obtaining the model molecules. For this purpose the general molecular structures which are used are as follows:

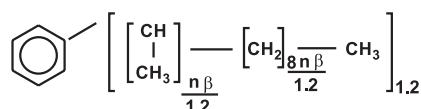
Paraffins:



Naphthenes:



Aromatics:



The last step is determining parameters  $n$ ,  $\alpha$ ,  $\beta$  in the above model molecules. To calculate these parameters the following system for conservation of mass must be solved:

$$(n+2)MW_{CH_3} + 8nMW_{CH_2} + nMW_{CH} = MW_{av,p} \quad (7)$$

$$4.8MW_{CH_2} + 1.2MW_{CH} + n\alpha MW_{CH-CH_3} + 8n\alpha MW_{CH_2} + 1.2MW_{CH_3} = MW_{av,n} \quad (8)$$

$$4.8MW_{CH} + 1.2MW_{CH_2} + n\beta MW_{CH-CH_3} + 8n\beta MW_{CH_2} + 1.2MW_{CH_3} = MW_{av,a} \quad (9)$$

Using the average molecular weights in the above system of equations leads to the following results:

$$n = 2.1298 \quad (10)$$

$$\alpha = 0.6407 \quad (11)$$

$$\beta = 0.5834 \quad (12)$$

It is worth noting that in this method the model molecules may have a noninteger number of groups in different hydrocarbon families. Now the complex mixture is considered to be consisted of these three model molecules. Therefore, the liquid-liquid equilibrium can be done. But as it can be seen from the structure of the model molecules, for calculating the activity coefficient of these molecules we must apply a group contribution method. In this work the UNIFAC model has chosen. In using this activity coefficient model, van der Waals surface and volume size parameters as well as the interaction parameters between different functional groups are required. Unfortunately, these parameters have not been reported for the groups involved in NMP [13], hence the application of UNIFAC model for the mixture contain NMP is not possible. To overcome this difficulty the size and energy parameters related to the NMP are calculated in the following form:

In the first step of this work we used Bondi's method [3] of functional groups for calculating van der Waals surface and volume size parameters of NMP, then the interaction parameters of NMP with the other groups in heptane and benzene were obtained. The idea of taking NMP as a functional group for obtaining the interaction parameters are based on similar works which have done by Mukhopadhyay and Dongaonkar [9] and Rahman et al. [12].

In the system of *n*-heptane/benzene/NMP two liquid phases are in equilibrium. The benzene rich phase is named extract and benzene lean phase is named raffinate. The condition for the equilibrium of these phases are

$$x_i^{(I)} \gamma_i^{(I)} = x_i^{(II)} \gamma_i^{(II)} \quad (13)$$

In which superscripts I and II refers to the first and second phases in equilibrium. In the UNIFAC model activity coefficient is represented as having two parts, i.e., combinatorial and residual activity coefficients:

$$\ln \gamma_i = \ln \gamma_i^{(c)} + \ln \gamma_i^{(R)} \quad (14)$$

The combinatorial part is given by the following equation:

$$\ln \gamma_i^{(c)} = (\ln \phi_i / x_i + l - \phi_i / x_i) - zq_i / 2 [\ln \phi_i / \theta_i + 1 - \phi_i / \theta_i] \quad (15)$$



$$x_i^I = \frac{\gamma_i^II x_i^II}{\gamma_i^I} \quad (33)$$

5. If  $\sum x_i^II = 1$  not satisfied,  $\phi$  is adjusted and Eqs. (32) and (33) are used again for  $x_i^II$  and  $x_i^I$ , respectively, until the equation  $\sum x_i^II = 1$  is satisfied.

**Table 3.** van der Waals surface area ( $Q$ ) and volume ( $R$ ) size parameters of the functional groups.

Groups	$R$	$Q$
CH <sub>2</sub>	0.6744	0.5400
CH <sub>3</sub>	0.9011	0.8480
ACH	0.5313	0.4000
NMP	3.9810	3.2000

**Table 4.** Functions ( $f_i$ ) and constants ( $C_i$ ) of the system of Eqs. (27–30).

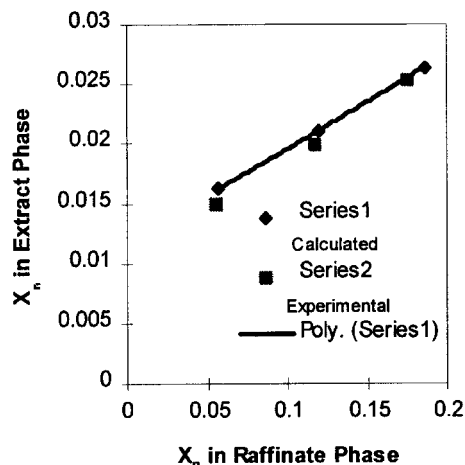
$C_1 = 0.3115$	$C_2 = 0.1894$
$C_2 = 0.1683$	$C_4 = 0.1447$
$f_1 = \frac{0.3346 + 0.6684\Psi_{41}}{0.8715 + 0.306\Psi_{41}}$	$f_{15} = \frac{0.4917 + 0.5128\Psi_{41}}{0.7873 + 0.2163\Psi_{41}}$
$f_2 = \frac{0.2503}{0.3346 + 0.6684\Psi_{41}}$	$f_{16} = \frac{0.3658}{0.4917 + 0.5128\Psi_{41}}$
$f_3 = \frac{-0.8151}{0.8715 + 0.306\Psi_{41}}$	$f_{17} = \frac{-0.6873}{0.7873 + 0.2163\Psi_{41}}$
$f_4 = \frac{0.06619}{0.2851 + 0.6684\Psi_{43}}$	$f_{18} = \frac{0.09881}{0.4193 + 0.5128\Psi_{43}}$
$f_5 = \frac{0.04427}{0.7183 + 0.1306\Psi_{43}}$	$f_{19} = \frac{0.07849}{0.6562 + 0.2163\Psi_{43}}$
$f_6 = \frac{0.6684\Psi_{14}}{0.6684 + 0.2503\Psi_{14} + 0.8125\Psi_{34}}$	$f_{20} = \frac{0.5128\Psi_{14}}{0.5128 + 0.3658\Psi_{14} + 0.1213\Psi_{34}}$
$f_7 = \frac{-0.1306 + 0.8151\Psi_{14} + 0.05435\Psi_{34}}{0.1306 + 0.8151\Psi_{14} + 0.05435\Psi_{34}}$	$f_{21} = \frac{-0.2163 + 0.6873\Psi_{14} + 0.09635\Psi_{34}}{0.2163 + 0.6873\Psi_{14} + 0.09635\Psi_{34}}$
$f_8 = \frac{0.4725 + 0.5321\Psi_{41}}{0.8047 + 0.1987\Psi_{41}}$	$f_{22} = \frac{0.5198 + 0.4849\Psi_{41}}{0.78 + 0.2237\Psi_{41}}$
$f_9 = \frac{0.3481}{0.4725 + 0.5321\Psi_{41}}$	$f_{23} = \frac{0.3925}{0.5198 + 0.4849\Psi_{41}}$
$f_{10} = \frac{-0.7082}{0.8047 + 0.1987\Psi_{41}}$	$f_{24} = \frac{-0.6741}{0.78 + 0.2237\Psi_{41}}$
$f_{11} = \frac{0.09759}{0.4034 + 0.5321\Psi_{43}}$	$f_{25} = \frac{0.09987}{0.4423 + 0.4849\Psi_{43}}$
$f_{12} = \frac{-0.07576}{0.6699 + 0.1987\Psi_{43}}$	$f_{26} = \frac{-0.0831}{0.6511 + 0.2237\Psi_{43}}$
$f_{13} = \frac{0.5321\Psi_{14}}{0.5321 + 0.3481\Psi_{14} + 0.1198\Psi_{34}}$	$f_{27} = \frac{0.4849\Psi_{14}}{0.4849 + 0.3925\Psi_{14} + 0.1226\Psi_{34}}$
$f_{14} = \frac{-0.1987\Psi_{14}}{0.1987 + 0.8395\Psi_{14} + 0.093\Psi_{34}}$	$f_{28} = \frac{-0.1987\Psi_{14}}{0.1987 + 0.8395\Psi_{14} + 0.093\Psi_{34}}$

**Table 5.** UNIFAC interaction parameters of different functional groups in ternary system of heptane/benzene/NMP.

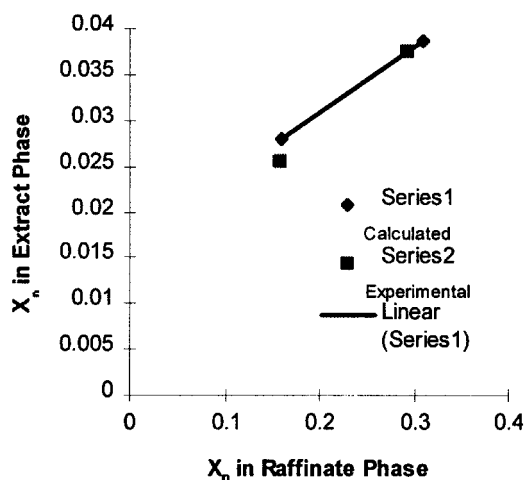
Groups	CH <sub>2</sub>	CH <sub>3</sub>	ACH	NMP
CH <sub>2</sub>	0	0	61.13	4833
CH <sub>3</sub>	0	0	61.13	4833
ACH	-11.12	-11.12	0	1262.5
NMP	-123.19	-123.19	-567.98	0

Calculated values for composition of liquid phases (extract and raffinate phases) and their experimental values have been

given in Tabs. 6 and 7 and their related ternary diagrams are shown in Figs. 2 and 3, respectively. As it can be shown in these figures the results of the calculations are in good agreement with the experimental data.



**Figure 2.** Distribution curve for the naphthenic components between the raffinate and extract phases at 1 atm and 50 °C.



**Figure 3.** Distribution curve for the naphthenic components between the raffinate and extract phases at 1 atm and 42 °C.

## 4 Conclusion

Although two well-known methods for characterization of complex hydrocarbon mixtures namely pseudocomponent and continuous methods have several important advantages such as simplicity for the first and time saving for the later, each of these methods have special deficiencies for the application to those thermodynamic calculations requiring the molecular characteristics of the different species in the complex multicomponent mixture. For example, in phase equilibrium calculations where the non-ideal behavior of components in the liquid phase must account for the activity coefficient. The properties such as the interaction parameters between different molecules in the mixture are needed which

**Table 6.** Calculated and experimental values of the composition of the extract and raffinate phases at 1 atm and 50 °C.

Experiments	Feed composition	Raffinate composition			Extract composition		
		Exp.	Calc.	AD	Exp.	Calc.	AD
<b>No. 1</b>							
$x_p$	.117	.451	.473	.022	.0396	.0412	.0016
$x_n$	.079	.175	.186	.011	.0254	.0264	.001
$x_a$	.042	.0561	.0591	.003	.0349	.0359	.001
$x_{NMP}$	.762	.317	.281	.036	.900	.896	.004
<b>No. 2</b>							
$x_p$	.102	.492	.501	.009	.0373	.0394	.0021
$x_n$	.0688	.117	.120	.003	.0199	.0211	.0012
$x_a$	.0369	.0697	.070	.0003	.0297	.0301	.0004
$x_{NMP}$	.793	.321	.309	.012	.913	.909	.004
<b>No. 3</b>							
$x_p$	.0661	.520	.531	.011	.0282	.0299	.0017
$x_n$	.0448	.0553	.0563	.001	.0150	.0162	.0012
$x_a$	.0240	.0818	.0830	.0012	.0205	.0216	.0011
$x_{NMP}$	.865	.343	.330	.013	.936	.932	.004
				AAD <sup>2</sup> = .0102			
					AAD = .0019		

1) AD = Absolute Deviation 2) AAD = Average Absolute Deviation

**Table 7.** Calculated and experimental values of the composition of the extract and raffinate phases at 1 atm and 42 °C.

Experiments	Feed composition	Raffinate composition			Extract composition		
		Exp.	Calc.	AD	Exp.	Calc.	AD
<b>No. 1</b>							
$x_p$	.117	.442	.454	.012	.0361	.0389	.0028
$x_n$	.079	.158	.160	.002	.0255	.0280	.0025
$x_a$	.042	.0532	.0549	.0017	.0322	.0344	.0022
$x_{NMP}$	.762	.346	.331	.015	.906	.899	.007
<b>No. 2</b>							
$x_p$	.101	.319	.334	.015	.0178	.0188	.001
$x_n$	.0685	.293	.310	.017	.0376	.0387	.0011
$x_a$	.0367	.0541	.0551	.001	.0301	.0314	.0013
$x_{NMP}$	.794	.334	.301	.033	.915	.911	.004
				AAD = .012			
					AAD = .0027		

is directly related to the molecular characteristics of the well-defined molecules in the mixture. To overcome the drawbacks of these methods from the molecular point of view, in this work the method of Ruzicka for modeling the complex mixture of hydrocarbons has been developed. In this method, the complex mixture of hydrocarbons which is comprised of the main homolog series of paraffins, naphthenes, and aromatics is modeled with the three representative molecules. Therefore, in this method a complex mixture is equivalent to a ternary mixture with defined molecules. Hence, we deal with a multicomponent mixture with a few components and the time for the calculation is less than the pseudocomponent method. On the other hand, the continuous method is not good enough to represent the mixtures which contain several homolog

series. For examination of the proposed method, the lube-oil cut SAE 10 of the Tehran Refinery is modeled and the results of this modeling along with the related liquid-liquid equilibrium calculations are in good agreement with the experimental data which are carefully obtained from the batch system of mixer-settler by the standard experimental measurements.

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### Symbols used

- $a_{mn}$  interaction parameter between  $m$  and  $n$  groups
- $MW$  molecular weight
- $N$  carbon number
- $q_i$  parameter in Eq. (15), defined in Eq. (19)
- $Q_k$  surface area parameter of the group  $k$
- $r_i$  parameter in Eq. (15), defined in Eq. (18)
- $R$  volume parameter
- $T$  absolute temperature
- $W(N)$  molecular distribution function
- $x_i$  mole fraction of the component “ $i$ ”
- $X_m$  parameter defined in Eq. (24)
- $z$  coordination number
- $\alpha$  parameter of the model molecules
- $\beta$  parameter of the model molecules
- $\gamma_i$  activity coefficient of the component “ $i$ ”
- $\Gamma_k$  group activity coefficient
- $\theta_i$  parameter in the Eq. (15), defined in Eq. (17)
- $\phi_i$  parameter in the Eq. (15), defined in Eq. (16)
- $\Psi_{mn}$  parameter defined in Eq. (22)
- $v_k$  number of group  $k$

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